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December 1989

Project 30.29.03
Piezoelectric Ceramics

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MINERAL SCIENCES LABORATORIES
DIVISION REPORT MSL 89-130 (IR)

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FTIR Spectral Studies on Gel Processed Modified $PbTiO_3$ Ceramics

By

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ABSTRACT

Precursor powders of a modified lead titanate composition containing Ca, Co and Mn as minor dopants have been synthesized using a gel processing technique. The powders were calcined in the temperature range of 100-800°C. The influence of heat treatment on the development of various phases has been monitored using both X-ray diffraction (XRD) and Fourier Transform Infrared (FTIR) spectroscopy. The study suggests that FTIR is a relatively simple and more sensitive technique than XRD and can be conveniently used to characterize precursor powders of the gel derived lead titanate based ceramics.

Keywords: Lead Titanate, Chemical Processing, FTIR,XRD measurements.

INTRODUCTION

The final properties in a ceramic product are often strongly influenced by the initial conditions used to synthesize and process the precursor powders. The characterization of the precursor powders is therefore of paramount importance for the development of advanced ceramic materials. Traditionally X-ray diffraction technique is employed to monitor the structural changes that occur as a result of the heat treatment of generally inorganic precursor raw materials. However XRD technique is not very effective when organic chemicals are used as precursor raw materials. As most of the organic as well as inorganic materials contain functional groups, having molecular vibrations in the infrared (i.r.) region of the electromagnetic spectrum, infrared spectroscopy can be conveniently applied to characterize them.

Conventionally dispersive infrared spectrometers have been employed to record the i.r. spectra of materials. These instruments are not very efficient as they normally use diffraction gratings to separate the different frequencies of light from the broad band i.r. source. In recent years dispersive infrared spectrometers are being replaced by instruments that utilize Michelson interferometers. These instruments operate by first collecting the data in the time domain and then computing the normal frequency spectra using Fourier transform, and are termed as

Fourier transform infrared Spectrometers. Unlike dispersive spectrometer the FTIR instrument keeps all the light together but modulates each frequency slightly differently, and as all the frequencies are monitored simultaneously there is a definite "multiplex" advantage over the dispersive instruments. The FTIR spectrometer offers greater speed, sensitivity, data accuracy and improved energy throughput compared to conventional dispersive instruments (1).

In this paper we describe the FTIR spectral studies on the precursor powders of a modified lead titanate composition prepared via gel processing technique. The FTIR spectra of the mixtures of the precursor raw materials in acetic acid solutions have also been recorded to follow the reaction sequence during the initial processing stages. Our interest in this material is because of its attractive properties e.g. high Curie temperature, low dielectric constant, low mechanical quality factor Q_m and the virtual absence of piezoelectric coupling in the transverse mode etc. These properties make it a potential candidate for under-water transducers at low frequency or for high frequency transducers for medical diagnostics and ultrasonic non-destructive testing of materials.

Conventionally, ceramic precursor powders are produced by mechanical mixing (ball milling or attrition milling) of the raw materials in the form of oxides or carbonates. These techniques are

plagued with inherent problems - e.g. inhomogeneous mixing, contamination due to grinding of the milling media, large particle size etc. A powder with relatively coarse particle size requires higher densification temperatures and the inhomogeneity in the precursor powders often results in the formation of undesired phases in the sintered body which may affect the final properties of the product adversely. The higher sintering temperatures are undesirable specially in the sintering of lead titanate based ceramics due to the greater evaporation of lead oxide that occurs at higher temperatures resulting in porous and non-stoichiometric sintered product.

Chemical routes for the processing of ceramic precursor powders offer several advantages e.g. greater control of chemical composition, homogeneity (as the mixing obtained in solutions is at the molecular or ionic scale), less contamination, ultrafine powders and other parameters necessary to produce high performance advanced ceramics. For example sol-gel processing has been successfully shown to produce inorganic precursors of enhanced quality (5-8).

This report describes a simple and unique gel processing method that has been developed at CANMET, to synthesize a modified lead titanate based ceramic material. The results from a detailed XRD and FTIR spectral study, conducted to monitor various structural changes that occur upon heat treatment of the gel

processed material are also discussed. The composition of the material investigated is given by the general formula:

$$[Pb_{1-x}Ca_x][(Co)_yMn_zTi_{1-y-z}]O_3$$

where

$$x \leq 0.35,\ y \leq 0.03 \text{ and } z \leq 0.02$$

EXPERIMENTAL PROCEDURES

A schematic diagram describing various steps used to synthesize modified lead titanate via gel processing technique is given in Fig. 1. In general appropriate amounts of precursor raw materials e.g., $PbCO_3$, Ca, Co and Mn acetates were dissolved in 80% aqueous acetic acid. Titanium-N-tetra butoxide (TNBT) also dissolved in 80% aqueous acetic acid, was then added dropwise to the above mixture to give a pink solution. This solution was evaporated in a rotary vacuum flask at ~40°C to form a viscous gel. The gel was subsequently precipitated in isopropanol and splat dried at 125°C to give bluish grey powders.

Powders were calcined in small batches (<10 g) in alumina crucibles loosely-covered with platinum foil at temperatures ranging from 100-800°C. The samples were kept at the desired temperature for a period of two hours and allowed to cool down to

room temperature by turning off the furnace. X-ray diffraction patterns for these powders were obtained using a Rigaku automated powder diffractometer with Cu-Kα radiation and a graphite monochromator. A Digilab model FTS40, FTIR spectrophotometer was used to obtain I.R. spectra of solids using lightly loaded (<1%) KBr-supported discs. FTIR spectra of liquids were produced using AgCl cells.

RESULTS and DISCUSSIONS

X-ray Diffraction Studies

The development of various phases in the gel-derived material as evidenced from XRD patterns showed strong dependence on the calcination temperatures, Fig. 2. The gel derived material was amorphous upto 360°C. At 500°C the perovskite lead titanate ($PbTiO_3$) phase was clearly observed along with trace amounts of orthorhombic lead oxide, PbO(O). Above 600°C, the $PbTiO_3$ phase structure was clearly resolved and trace amounts of orthorhombic PbO were still detectable. Heat treatment to 700°C resulted in the disappearance of the orthorhombic PbO phase and the formation of well developed lead titanate along with trace amounts of tetragonal lead oxide phase PbO(T). Further increase in calcination temperature to 800°C produced single phase lead titanate material.

FTIR Studies

The FTIR spectra of the major components e.g. $PbCO_3$, $PbCO_3$+$CaCO_3$ and $PbCO_3$+$CaCO_3$+TNBT in aqueous acetic acid solution were recorded to follow the reaction sequence during gel processing. Fig. 3 shows the solution FTIR spectra of these components in aqueous acetic acid. It is evident that the three spectra are dominated by the acetate ions. The broad absorption bands around 3400 cm^{-1} are due to stretching vibrations of the -O-O-H, hydrogen bonds. The multiple bands around 2900 cm^{-1} could be assigned to the stretching vibrations of the acetate ions. The rather broad peak at around 2600 cm^{-1} is presumably the combination band for the acetate ions. This assignment is compatible with the corresponding assignment for the sodium acetate ions made by Ito et. al (6). The strong band around 1700 cm^{-1} is typical of the C=O stretching vibration of the acetic acid that normally exists as a dimer. The carboxylate ion (COO^-) asymmetric stretch vibrations O-C-O appear around 1550 cm^{-1} and the symmetric vibrations are observed at about 1400 cm^{-1}. A shoulder band around 1350 cm^{-1} is due to the CH_3 deformation vibrations. Similar assignments have been previously reported for the other acetate complexes (6,7). The intense peak around 1270 cm^{-1} is characteristic of the C-O stretching vibration of the carboxylic acid dimer. The bands around 1050-1100 cm^{-1} are due to the CH_3-C rocking vibration. The peaks between 850-1050 cm^{-1} cannot be assigned to C-C stretching vibrations, since in acetates these vibrations are not infrared active (8). These bands could be due to the metal-acetate bonding and O-H deformation

vibrations.

The powder FTIR spectra of the intended composition processed by the gel technique and calcined at temperatures ranging from 150-800 °C are shown in Fig. 4-6. Heat treatment of the dried powder (obtained via rotary evaporation of the solution) to 120°C resulted in the reduction of relative band intensities corresponding to O-H, C-H, C=O and C-O stretching vibrations (at 3400, 2900, 1700 and 1270 cm^{-1} respectively) due to the partial loss of water and acetic acid from the material. The loss of acid/water also improved the resolution of the remaining peaks in the 1000-1600 cm^{-1} region. The broad band near 800 cm^{-1} is typical of metal-oxygen bonding and the peak centred around 625 cm^{-1} could be due to COO out-of-plane rocking vibration. The bands in the 400-600 cm^{-1} region are probably due to various skeletal and COO in-plane vibrations.

Heat treatment of the gel derived powders to 300°C resulted in almost complete disappearance of the peaks corresponding to C-H, C=O, C-O and COO functional groups indicating the decomposition of organic materials. The band around 1450 cm^{-1} could be a combination of carbonyl absorption due to metal carbonate and residual carboxylate ion. DTA studies (9) also support the formation of carbonates at this temperature. The broad absorption bands in the 300-600 cm^{-1} region are typically due to metal-oxygen bonding. It is interesting that the hydroxyl group peaks (at ~3400 and 1600 cm^{-1} respectively) still exist in powders dried at 300°C. This could be

due to the moisture absorption by particles having very high surface area as discussed in the previous section. The spectral features at 400 and 500°C are similar to those observed at 300°C except that the bands due to metal-carbonate and metal oxygen bonding are more clearly resolved and the O-H stretching vibration band is reduced in intensity. At 600°C the carbonate ion peak at ~1450 cm^{-1} is significantly reduced in intensity and the metal-oxygen peaks at ~400 and 600 cm^{-1} characteristic of lead titanate material (10) are quite apparent. At 800°C the carbonate ion peak (~1450 cm^{-1}) is no more visible indicating the complete decomposition of carbonates into oxides and the subsequent formation of $PbTiO_3$ based product. Only well resolved lead titanate peaks suggesting the formation of single phase material are present at this temperature.

CONCLUSIONS

The results from the XRD studies indicate that, gel processing can produce highly reactive precursor powders that can provide virtually single phase lead titanate powders at temperatures above 500°C . Precursor powders prepared by conventionally ball-milled or attrition milled powders display significant amounts of impurity phases even up to temperatures as high as 800°C (11). This suggests that gel processed material will require lower sintering temperatures to form dense ceramic bodies. The lower sintering

temperatures are highly desireable for the sintering of $PbTiO_3$ based ceramics, as it reduces the problems associated with PbO evaporation that can cause inhomogeneity in the sintered product. The FTIR data, however indicates the presence of metal-carbonates even at 600°C. This suggests that FTIR is relatively a more sensitive technique than XRD for the characterization of these powders. The FTIR spectral studies also indicate that at lower temperatures <300°C, the gel derived materials are dominated by the presence of acetate ions. Above 300°C the organics decompose to form the metal carbonates. Further heat treatment to 500°C results in the decomposition of metal-carbonates to form lead titanate based product.

ACKNOWLEDGEMENTS

The authors acknowledge the technical assistance of Ms. K. Besso and Mr. P. Carriere of the Mineral Sciences Laboratories (MSL), CANMET/E.M & R for providing XRD data on the powders and Mrs. V. Rolko also of MSL, for recording some of the FTIR spectra.

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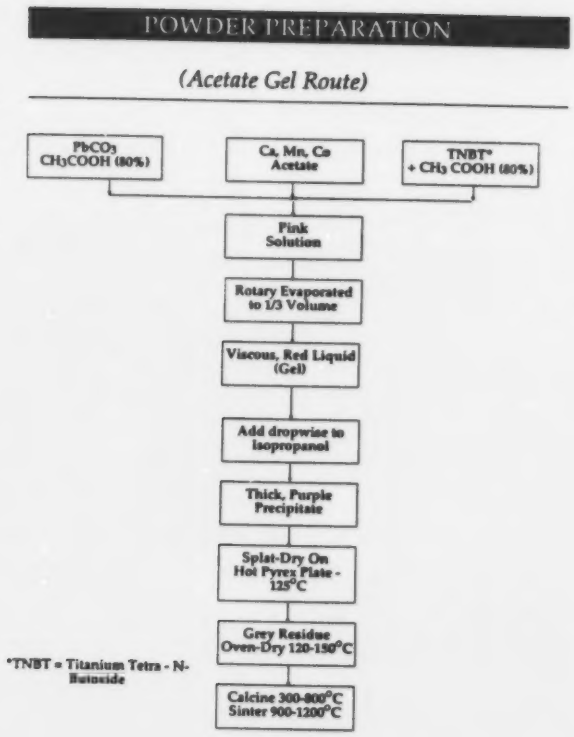
POWDER PREPARATION
(Acetate Gel Route)
PbCO3 CH3COOH (80%)
Ca, Mn, Co Acetate
TNBT* + CH3 COOH (80%)
Pink Solution
Rotary Evaporated to 1/3 Volume
Viscous, Red Liquid (Gel)
Add dropwise to Isopropanol
Thick, Purple Precipitate
Splat-Dry On Hot Pyrex Plate - 125°C
Grey Residue Oven-Dry 120-150°C
Calcine 300-800°C Sinter 900-1200°C
*TNBT = Titanium Tetra - N-Butoxide

Fig. 1. A schematic diagram for the synthesis of modified lead titanate via gel processing route.

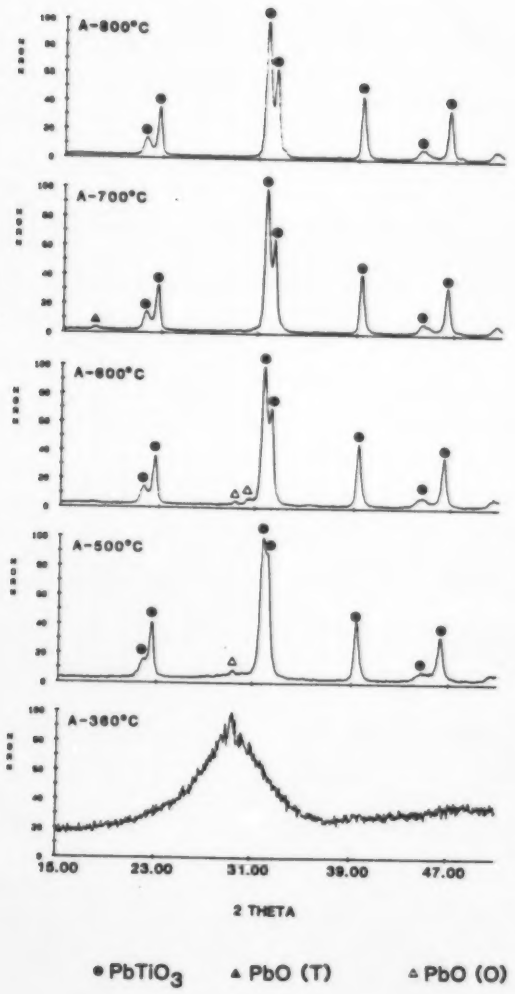

Fig. 2. X-ray diffraction patterns of gel-derived $PbTiO_3$ powders at various temperatures.

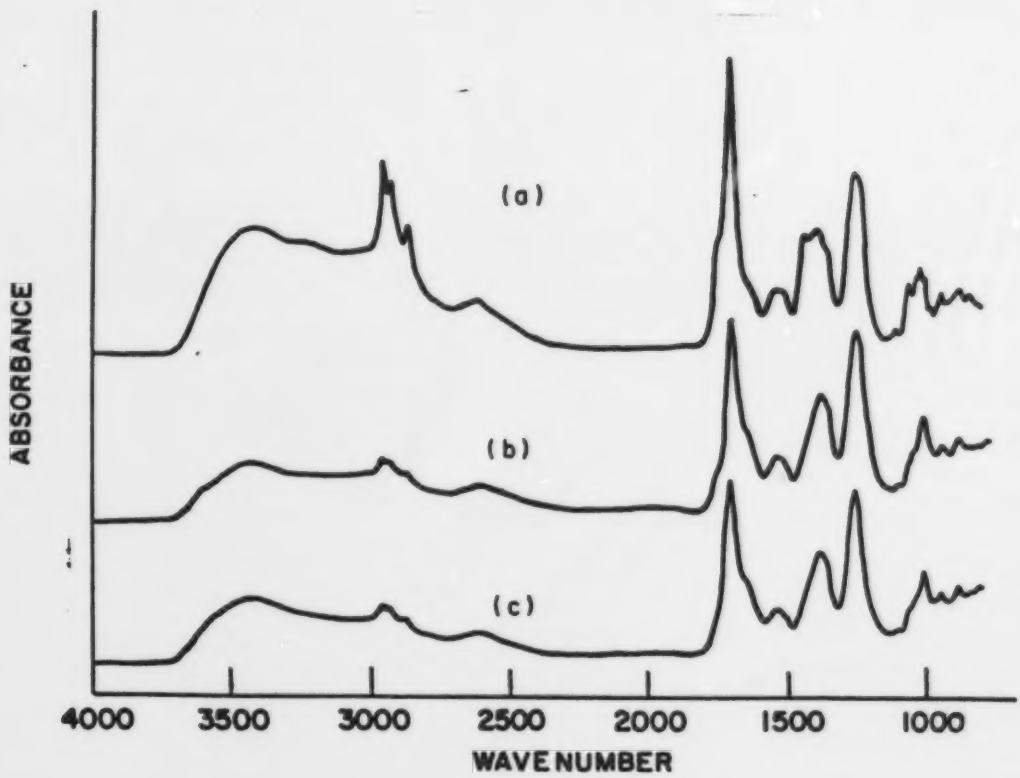

Fig. 3. FTIR spectra of (a) $PbCO_3$ (b) $PbCO_3$+$CaCO_3$ and (c) $PbCO_3$+$CaCO_3$+TNBT in acetic acid solution at room temperature.

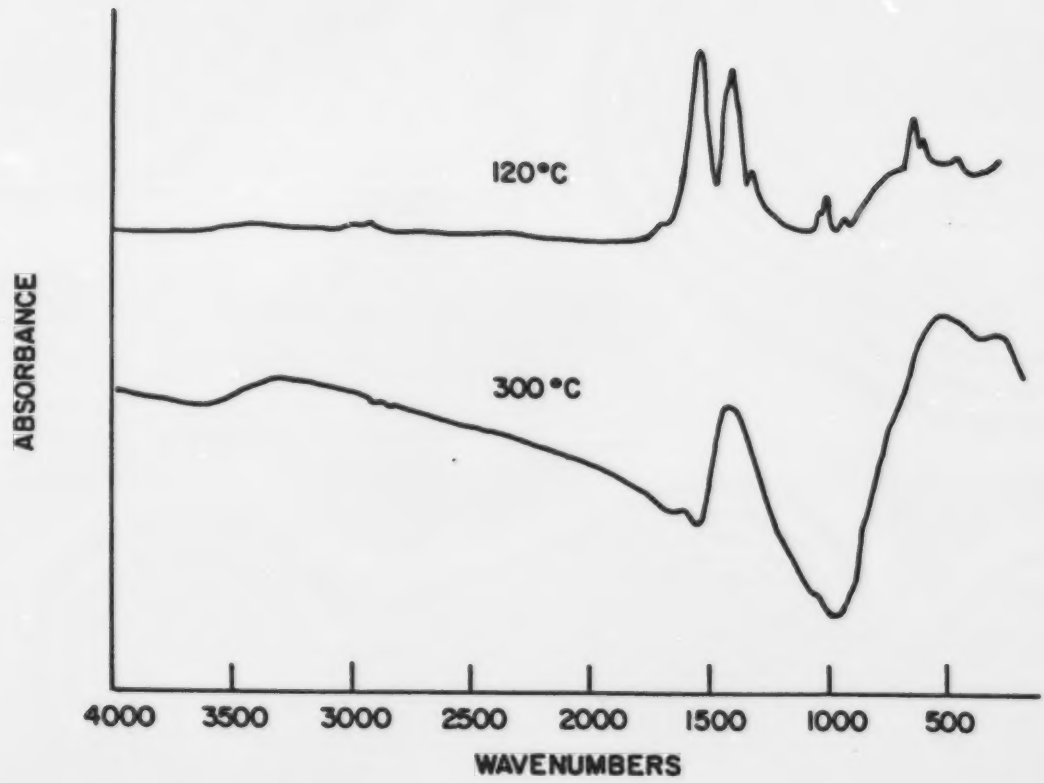

Fig. 4. FTIR spectra of the gel derived powders heat treated to 120°C and 300°C.

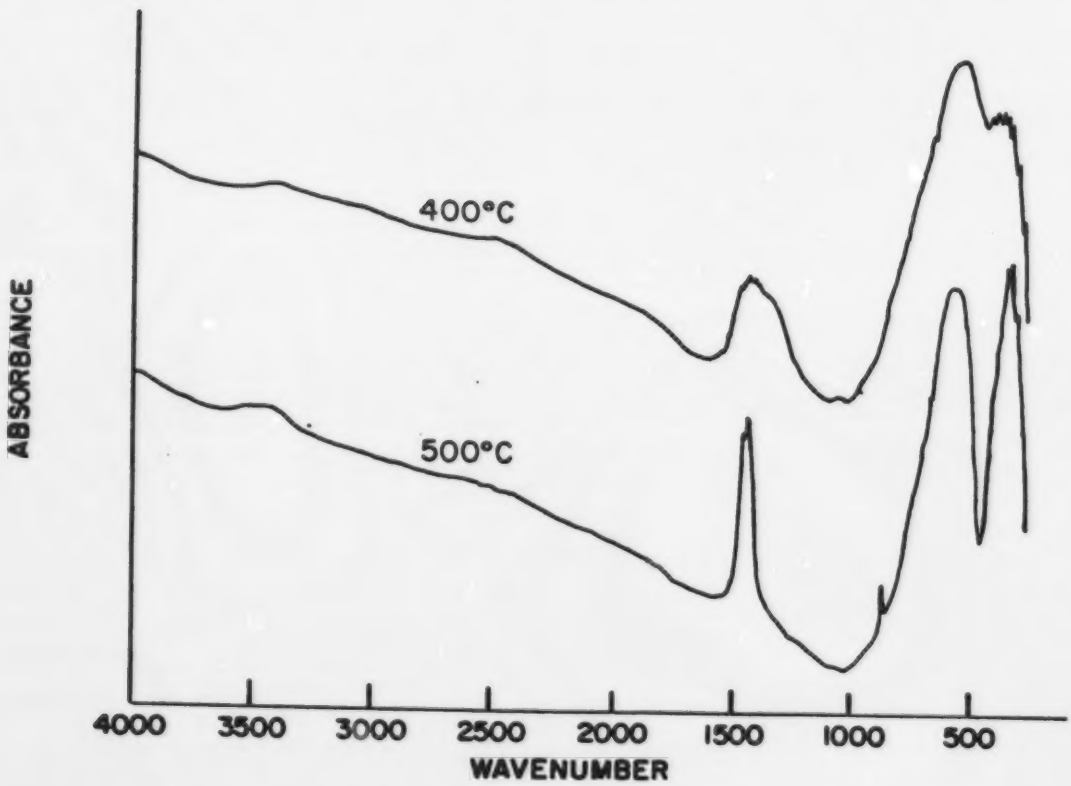

Fig. 5. FTIR spectra of the gel derived powders heat treated to 400°C and 500°C.

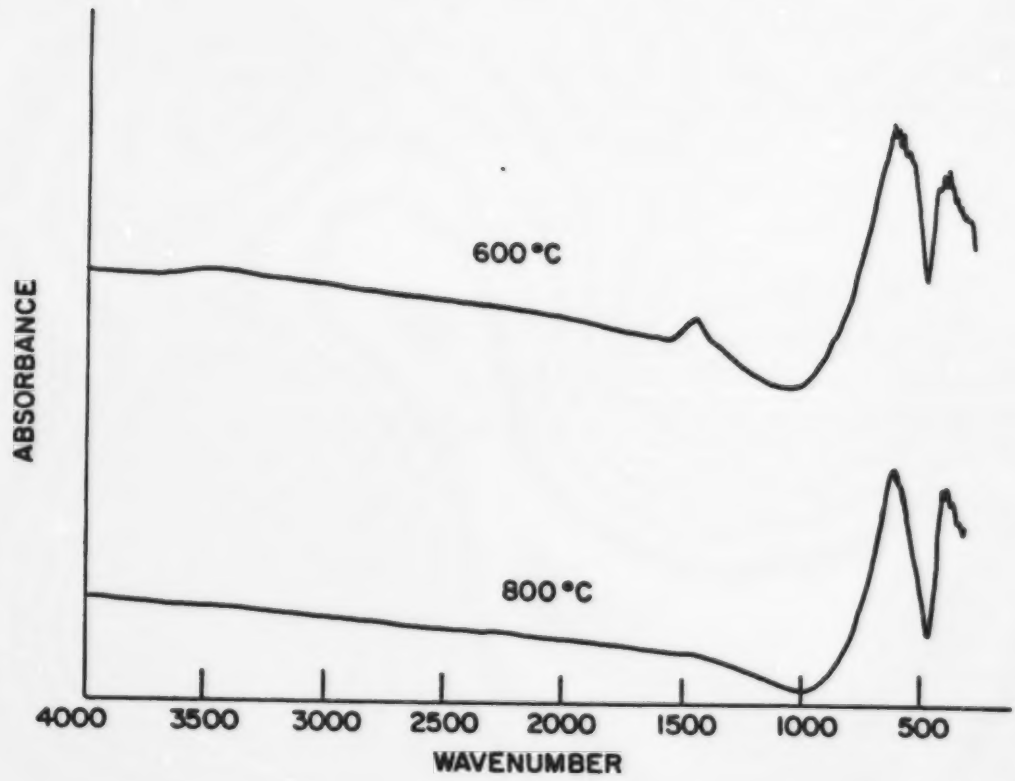

Fig. 6. FTIR spectra of the gel derived powders heat treated to 600°C and 800°C.